

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : D21C 9/16		A1	(11) International Publication Number: WO 93/14262 (43) International Publication Date: 22 July 1993 (22.07.93)
(21) International Application Number: PCT/SE93/00012 (22) International Filing Date: 12 January 1993 (12.01.93)		(74) Agent: SUNDQVIST, Hans; Sunds Defibrator Industries Aktiebolag, Strandbergsgatan 61, S-112 51 Stockholm (SE).	
(30) Priority data: 9200152-8 21 January 1992 (21.01.92) SE		(81) Designated States: AU, BR, CA, FI, JP, NO, NZ, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(71) Applicant (for all designated States except US): SUNDs DEFIBRATOR INDUSTRIES AKTIEBOLAG [SE/SE]; S-851 94 Sundsvall (SE). (72) Inventors; and (75) Inventors/Applicants (for US only): LINDSTRÖM, Lars-Åke [SE/SE]; Skonertvägen 18 S-860 24 Alnö (SE); SJÖDIN, Lars [SE/SE]; Spårvägen 5, S-852 41 Sundsvall (SE); NORDEN, Solveig [SE/SE]; Odalvägen 14, S-860 20 Njurunda (SE); DAHL, Mårten [SE/SE]; Ludvigsbergsvägen 30, S-852 34 Sundsvall (SE).		Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	

(54) Title: BLEACHING OF CHEMICAL PULP

(57) Abstract

A method of bleaching sulphate pulp without using chlorine-containing bleaching agents. The sulphate pulp is oxygen delignified and can possibly also be ozone delignified to a kappa number below 9.5. Thereafter a pretreatment with complexing agent is carried out for 1-60 minutes, at which the pulp consistency is 1-15 %, the temperature 70-110 °C and pH 5-7. The pulp thus pretreated is washed and dewatered to a consistency of 18-40 %. Thereafter peroxide bleaching in alkaline environment takes place in the presence of silicate or an organic complexing agent of the type phosphonic or carboxylic acid.

$\text{O} - \text{Z} - \text{Q} - \text{W} - \text{P}$
pH 5-7
70-110°C
CuO
18-40%

Bleaching of chemical pulp

This invention relates to the bleaching of sulphate pulp without using bleaching agents containing chlorine. The technique of bleaching chemical pulps is now developing rapidly, because the bleaching chemicals heretofore mainly used, Cl_2 , ClO_2 , and hypochlorite, are feared to give rise to products being a risk for the environment and health.

Until now, the discussions have been concentrated on the emissions of chlorinated organic substance to the recipient. The majority of the countries in the world have now established limit values for these emissions, which normally are measured as AOX (Adsorbable organic halogens). As a new trend, the customers require to an ever increasing degree paper with a low content of chlorinated organic substance.

Conventional bleaching with Cl_2 disappears now more and more, and Cl_2 is replaced primarily by ClO_2 . Bleaching with ClO_2 causes substantially lower AOX-emissions to the recipient, but the amount of chlorinated substance in the pulp is affected only insignificantly.

In recent years, the use of hydroperoxide at the bleaching of chemical pulps has increased considerably. Hydroperoxide can replace part of the chlorine chemicals.

In patent application SE 89 02058-0, a method is described at which the pulp is pretreated with complexing agent under neutral conditions. By this process, coniferous sulphate pulp can be bleached with peroxide-containing bleaching agents to 70-75% ISO at about 10% pulp consistency. In order to achieve fully bleached pulp qualities with higher ISO-brightness (above 83% ISO), this process can be combined with final bleaching with ClO_2 . As a result, this final bleaching then yields emission of AOX from the bleach plant and chlorinated organic substance in the bleached pulp.

Other known methods of reducing emissions of chlorinated organic substance to the recipient are to extend the delignification further in the closed part of the mill, i.e. in the digester house and/or oxygen step.

Extended digestion with maintained pulp quality can be achieved by impregnating the chips with black liquor in the initial phase of the cook, as described in Finnish patent application 90 0663. This method renders it possible to digest pulp down to a kappa number of about 10 and obtain strength properties equal to or better than with pulp digested to conventional level, kappa number 25-30. Combined with oxygen delignification, kappa numbers as low as 5-6 can be obtained for further bleaching.

By combining conventional digestion, oxygen delignification and ozone bleaching in acid environment, kappa numbers lower than 10 can be obtained.

It has, however, not been possible to produce fully bleached pulp qualities without final bleaching with ClO_2 .

The present invention implies, that fully bleached pulp with a brightness above 83% ISO can be made without the use of chlorine-containing bleaching agents.

At the start of the bleaching, the pulp shall have a kappa number below 9.5. This can be achieved by conventional or extended digestion followed by O_2 -delignification, alternatively by conventional or extended digestion followed by O_2 - and O_3 -delignification. The bleaching is initiated by a pretreatment step with complexing agent followed by treatment with hydroperoxide in alkaline environment in the presence of silicate or an organic complexing agent of the type phosphonic or carboxylic acid.

The characterizing features of the invention are apparent from the attached claims.

The pulp digested and delignified with oxygen and possibly ozone according to above shall have a kappa number below 9.5. This can be achieved by known methods of digestion and delignification. The pulp shall thereafter be pretreated with complexing agent, for example EDTA or DTPA, at a pulp consistency of 1-15% for 1-60 minutes, preferably 5-30 minutes. The temperature shall be 70-100°C, preferably 80-100°C, and the pH-value 5-7.

The pulp thus pretreated is washed and dewatered to a consistency of 18-40%, preferably 20-30%. The pH-value is increased to alkaline level, and hydroperoxide is added together with silicate, for example sodium silicate, alternatively together with an organic complexing agent of the type phosphonic or carboxylic acid. The dwell time of the pulp in this hydroperoxide step shall be 1/2 - 5 hours, preferably 1-4 hours, and the temperature 70-100°C, preferably 80-100°C. The silicate charge shall be 2-30 kg/ton pulp, preferably 5-15 kg/ton pulp, expressed as SiO₂. Alternatively, the charge of the organic complexing agent shall be 0.5-5 kg/ton pulp.

Fig. 1 is a diagram, in which the brightness of the pulp is plotted as a function of the pulp consistency at the peroxide bleaching, partly at conventional peroxide bleaching and partly at bleaching according to the invention. The starting pulp was oxygen-delignified coniferous wood sulphate pulp with kappa number 6.5 (10.5 after digestion). Curve 1 shows conventional peroxide bleaching, with a consumption of H₂O₂ of 20 kg/ton pulp. Curve 2 and, respectively, 3 refer to bleaching according to the invention with silicate addition and a consumption of H₂O₂ of 20 and, respectively, 30 kg/ton pulp.

It appears from the diagram how the brightness, after bleaching according to the invention and, respectively, after conventional bleaching, depends on the pulp consistency. At about 12% pulp consistency, the brightness obtained is equal in both cases, but at increased pulp consistency in the peroxide step an increased brightness is obtained according to the invention, while conventional peroxide bleaching results in a deteriorated brightness.

The following examples have the object to additionally elucidate the invention and its advantages.

Example 1

An oxygen-dé lignified coniferous wood sulphate pulp (Scandinavian fir/pine) with kappa number 6.4 (10.5 after digestion according to above Finnish patent application 90 0663), brightness 43% ISO, intrinsic viscosity 605 dm³/kg, was pretreated with complexing agent and peroxide bleached according to the invention.

Pretreatment

Pulp consistency	%	5
Time	min	15
Temperature	°C	90
EDTA	kg/ton	2
Final pH		6.1

Peroxide step

Pulp consistency	%	25
Time	min	240
Temperature	°C	90
SiO ₂	kg/ton	10
H ₂ O ₂ consumption	kg/ton	13.5 32.0
Final pH		10.2 10.3
Brightness	% ISO	79.6 84.2
Intrinsic viscosity	dm ³ /kg	520 447

Example 2

A coniferous wood sulphate pulp with kappa number 13.3 (digested of Scandinavian fir/pine according to Finnish patent application 90 0663), oxygen delignified to kappa number 8.3: and ozone bleached in acid environment to kappa number 3.2, brightness 61% ISO, intrinsic viscosity 582 dm³/kg, was bleached according to the invention.

Pretreatment as in Example 1

Peroxide bleaching

Pulp consistency	%	25		
Time	min	240		
Temperature	°C	90		
SiO ₂	kg/ton	10		
H ₂ O ₂ consumption	kg/ton	7.3	14.2	30.1
Final pH		8.9	9.5	10.1
Brightness	% ISO	85.3	88.4	90.4
Intrinsic viscosity	dm ³ /kg	536	498	420

Example 3

An oxygen delignified coniferous wood sulphate pulp (digested of Pinus taeda according to Finnish patent application 90 0663) with kappa number 9.9, ozone bleached to kappa number 4.8, brightness 54.5% ISO, intrinsic viscosity 607 dm³/kg was pretreated and bleached according to the invention.

Pretreatment as in Example 1

Peroxide bleaching

Pulp consistency	%	25		
Time	min	240		
Temperature	°C	90		
SiO ₂	kg/ton	10		
H ₂ O ₂ consumption	kg/ton	7.9	14.6	29.6
Final pH		10.2	10.4	10.6

Brightness	% ISO	81.3	85.3	87.8
Intrinsic viscosity	dm ³ /kg	570	534	459

Example 4

An oxygen delignified birch sulphate pulp with kappa number 9.0, brightness 59.4% ISO and intrinsic viscosity 996 dm³/kg was bleached according to the invention.

Pretreatment as in Example 1

Peroxide bleaching

Pulp consistency	%	25		
Time	min	240		
Temperature	°C	90		
SiO ₂	kg/ton	10		
H ₂ O ₂ consumption	kg/ton	8.5	17.5	35
Final pH		10.2	10.4	10.5
Brightness	% ISO	82.2	85.5	86.5
Intrinsic viscosity	dm ³ /kg	903	975	822

The invention is not restricted to the embodiments set forth above, but can be varied within the scope of the invention idea.

Claims

1. A method of bleaching sulphate pulp without using chlorine-containing bleaching agents, comprising oxygen delignification and possibly ozone delignification of the pulp to a kappa number below 9.5 and subsequent peroxide bleaching, characterized in that the pulp directly after the delignification is pretreated with complexing agent for 1-60 minutes, the pulp consistency being 1-15%, the temperature 70-110°C and pH 5-7, and that the pulp thus pretreated is washed and dewatered to a consistency of 18-40% and thereafter peroxide bleached in alkaline environment in the presence of silicate or an organic complexing agent of the type phosphonic or carboxylic acid.
2. A method as defined in claim 1, characterized in that the peroxide bleaching is carried out for 1/2-5 hours at the temperature 70-110°C.
3. A method as defined in claim 1 or 2, characterized in that as complexing agent at the pretreatment EDTA or DTPA is used.
4. A method as defined in any one of the preceding claims, characterized in that at the peroxide bleaching silicate is added in an amount of 2-30 kg/ton pulp, expressed as SiO₂.
5. A method as defined in any one of the claims 1-3, characterized in that at the peroxide bleaching an organic complexing agent of the type phosphonic acid or carboxylic acid is added in an amount of 0.5-5 kg/ton pulp.
6. A method as defined in any one of the preceding claims, characterized in that the bleaching is carried out to a brightness exceeding 83% ISO.

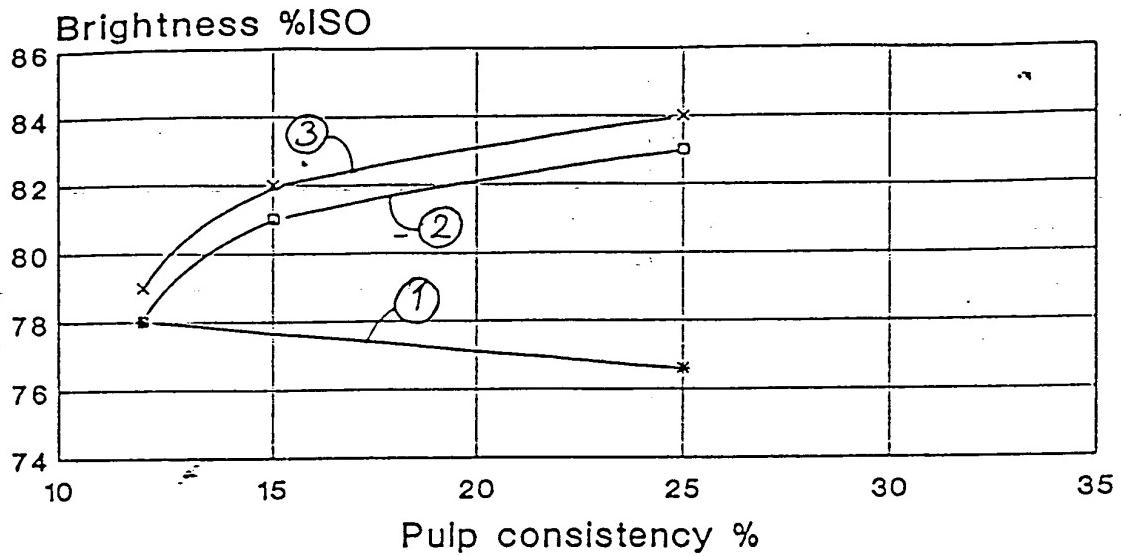


Fig 1

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: D21C 9/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, A2, 0402335 (EKA NOBEL AKTIEBOLAG), 12 December 1990 (12.12.90), page 3, line 38 - page 4, line 15 --	1-6
A	JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, Volume 2, No 3, 1982, Göran Gellerstedt et al, "CHEMICAL ASPECTS OF HYDROGEN PEROXIDE BLEACHING", page 231 - page 250, esp. page 233, line 29 - line 33 --	1-6
A	EP, A1, 0262836 (THE DOW CHEMICAL COMPANY), 6 April 1988 (06.04.88), page 4, line 36 - page 5, line 43 --	1-6

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "B" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

6 May 1993

Date of mailing of the international search report

10 -05- 1993

Name and mailing address of the ISA/
Swedish Patent Office
Box 5055, S-102 42 STOCKHOLM
Facsimile No. +46 8 666 02 86

Authorized officer

Marianne Bratsberg
Telephone No. +46 8 782 25 00

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim
A	US, A, 4938842 (PHILIP WHITING ET AL), 3 July 1990 (03.07.90), column 2, line 4 - line 38	1-6
A	WO, A1, 9112368 (SUNDS DEFIBRATOR RAUMA OY), 22 August 1991 (22.08.91), page 5, line 33 - page 6, line 3	1-6

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A2- 0402335	12/12/90	AU-B-	613272	25/07/91
		AU-A-	5621790	07/02/91
		CA-A-	2017807	06/12/90
		JP-A-	3027191	05/02/91
		SE-B,C-	467006	11/05/92
		SE-A-	8902058	07/12/90
EP-A1- 0262836	06/04/88	SE-T3-	0262836	
		AU-B-	600756	23/08/90
		AU-A-	7840787	17/03/88
		CA-A-	1284558	04/06/91
		DE-A-	3775688	13/02/92
		JP-A-	63120187	24/05/88
		US-A-	4732650	22/03/88
US-A- 4938842	03/07/90	CA-A-	1281855	26/03/91
WO-A1- 9112368	22/08/91	AU-A-	7218991	03/09/91
		EP-A-	0468016	29/01/92